Chemicals from Coal Hydrogenation Products

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## INTRODUCTION

Coal has been the source of large quantities of useful chemicals and will continue to be for a long time to come. Because coal is a major resource of our country, the Federal Bureau of Mines is vitally concerned with its development and efficient utilization. Although millions of pounds of coal chemicals are marketed each year, people working with coal envision an even greater potential as new processes are developed. The discussion that follows will consider some of the methods that have occupied the minds of men for some time and some of the recent developments pioneered by the Bureau.

The coal hydrogenation process for making liquid fuels has been investigated in detail since its application as an industrial process almost 40 years ago. As time passed economic and technical changes have taken place that justify a reevaluation of existing knowledge. Under present quasi-peaceful world conditions where a copious supply of natural petroleum is available at low cost, hydrogenation of coal cannot be considered as a major source of liquid fuels.[5] However, coal is an abundant raw material, and its application to other processes, exclusive of power and heat generation, presents a real challenge. Organizations in the United States and abroad have investigated the hydrogenation of coal and other coal utilization processes for many years. This work is still in progress in varying degrees, and in the following discussion are some of the gaseous, liquid, and solid chemicals that can be derived from the hydrogenation of coal. Associated with these technical developments are many design problems and an ever changing economic situation.

## DISCUSSION

When considering the utilization of coal, it is natural to think in terms of thousands or even millions of tons a year. If the potential chemical products from coal are estimated, the quantities of chemicals must be evaluated in terms of present and potential markets. The tonnages of possible products are high and in some instances are greater than the current usage. Table 1 is a list of the more voluminous products that could be produced in a single 30,000-bbl/day coal hydrogenation plant that reacts about 12,000 tons of coal per day. These facts are fairly well known, and rather than recite comparative figures, consideration will be given to some of the more plentiful chemicals. It should be mentioned that there is considerable process flexibility to change the product distribution.

The potential yield of most chemicals from hydrogenation is several times greater than from carbonization since most of the carbon is converted to liquid and gaseous hydrocarbons. The list of potential chemicals from coal hydrogenation is extensive and generally can be categorized by the type of compounds shown in figure 1. Products of coal hydrogenation contain appreciable quantities of aliphatics, aromatics (single-ring and polycyclic), substituted aromatics, heterocyclic compounds, and hydroaromatics. Many of the products that can be produced in quantity have only limited markets, and their disposal could be a problem.[4], [7]

TABLE 1.- Chemicals from a Coal Hydrogenation Plant
(30,000 barrels per day from Illinois coal)

| Aromatics | Million pounds per year[a] | |
|---|---|---|
| Benzene ................. | 224 | (4,000)[b] |
| Toluene ................. | 372 | (1,875) |
| Xylene .................... | 425 | (1,880) |
| Ethylbenzene ............. | 73 | - |
| Naphthalene .............. | 104 | ( 497) |
| Mixed aromatics .......... | 175 | |
| Total .............. | 1,373 | |

| Tar acids | | |
|---|---|---|
| Phenol ................... | 51.8 | |
| o-Cresol ................. | 5.8 | |
| m-, p-Cresol ............. | 63.3 | |
| Xylenols ................. | 44.8 | |
| Total .............. | 165.7 | |

| | | |
|---|---|---|
| Ammonium sulfate, tons/year ... | 148,500 | |
| Sulfuric acid, tons/year ...... | 29,400 | |

a/  330 stream days.
b/  1961 production from all sources in parentheses, million pounds
per year.

It would be desirable to be able to produce and separate only compounds for which there is a ready market. In this way, salable products would not have to bear the burden of chemicals that have only fuel value.

At the present time the most useful products from coal are the low-molecular-weight members of each series; benzene, toluene, xylene, naphthalene, and phenol. These are the preferred elementary building blocks used to make well-defined products. Plastics, synthetic fibers, resins, detergents, and elastomers consume 7.3 billion pounds a year of benzene, toluene, and xylene, 520 million pounds of naphthalene, and 780 million pounds of phenol. The consumption of these five major raw materials that can be made from coal is still growing. So far, no one has been able to justify the investment in a coal hydrogenation system to produce the few marketable products. In fact, the direction in recent years has been to dealkylate substituted aromatics from petroleum, producing benzene and naphthalene for consumption in synthesis indus-tries.[1] Here is a case where knowledge of the product composition and process know-how were applied to supply a need as the market developed beyond the capacity of the primary sources.

In 1952 Chemical and Engineering News[3] described studies by Carbide and Carbon Co. and its "coal hydrogenation unit designed to manufacture aromatic chemicals." Carbide and Carbon did much work on the primary liquefaction products and found a large number of chemicals worth up to several dollars a pound. Some of the products visualized as finished products of intermediates were the light products B-T-X, naph-thalene, and tar acids and heavier useful materials such as indan, fluorene, anthra-cene, phenanthrene, indanols, quinoline, carbazole, furans, and many others. These are indicated in the figure described previously. Markets have not developed for most of the high-molecular-weight products that could be separated. Instead, the demand con-tinues to increase for lower-molecular-weight chemicals as monomers for designing com-plex molecules that have no structural counterpart in the hydrogenation products.

Condensed aromatic structures such as pyrene and coronene, which may be considered as useful products, are resistant to mild hydrogenation conditions. They are recovered in the heavy oil product from hydrogenation of coal and can be isolated in a crystalline form. The greatest amount of condensed aromatics are recovered in "kiln oil" produced by roasting the plant residue. Actually, condensed aromatics are formed in the kiln through cracking and dehydrogenation during carbonization. Other components of the recovered oil are methylpyrenes, carbazole, and some 1,12 benzperylene.

Pyrene, which may be in 10 to 12 percent concentration in the kiln oil, can be concentrated further by distillation and isolating the mid-40-percent fraction. Carbazole is concentrated in the low-boiling fraction, and the vacuum residue contains the coronene concentrate. The pyrene fraction is distilled into narrow fractions separated from the oil and mixed with a solvent such as benzene-alcohol that dissolves only oil. When the solvent is centrifuged or filtered off, pure pyrene remains.

Carbazole is very resistant to hydrogenation, and most other aromatics in the low boiling fraction of the kiln oil can be hydrogenated to lighter distillable oils. The remaining carbazole is insoluble and can be separated by filtration and distillation.

Coronene can be isolated from the kiln oil residuum after vacuum distillation to remove pyrene. The fraction boiling at 350° to 400° C is slurried with benzene and filtered. Coronene is insoluble and is recovered in pure form. Contaminating hydrocarbons can be hydrogenated to lower boiling liquids by catalytic refining. Coronene is not hydrogenated and is recovered as a precipitate. Further purification can be done by vacuum distillation or recrystallyation from o-dichlorobenzene.

Small-scale studies on the hydrogenation of coal have been limited in the past by the relatively long time, 3 to 4 hours, required to heat and cool in autoclave. The influence of temperatures, especially above 350° C, on the experimental results has always raised questions concerning the validity of the data. The reaction system shown in figure 3 was developed with two main objectives, rapid heating and cooling and small charge size. Passing a low voltage and high current (about 700 amps at 15 v) through the type 304 stainless steel reactor raises the temperature to 800° C in about 2 minutes. Pressures as high as 6,000 psig could be maintained for over an hour before metal fatigue occurred. When an experiment is completed, the reactor is cooled in about 10 seconds by a water jet. Details of this apparatus have been published.[9] Experiments on the hydrogenation of coal could then be made at more severe conditions for the production of methane and light hydrocarbons, and from these studies a new synthesis of polycyclic aromatics was found.

If dry coal is hydrogenated at 6,000 psig and 800° C for zero and 15 minutes and a hydrogen rate of 100 scfh (0.5 fps), the results shown in figures 4 to 6 are obtained.[8] In general, the conversion of all coals is most rapid within the first 3 minutes and thereafter proceeds at a steady, slower rate. The yield of gas is similiar but there is no change in the yield of liquids which are produced in the early stage of the reaction and swept out of the apparatus. This reaction is substantiated by the comparative experiments shown in figure 7, where two sets of experimental data made at two gas velocities are shown. At the lower gas rate of 20 scfh the hydrocarbon vapors have more time to be hydrocracked to additional hydrocarbon gases.

The concentration of methane in the $C_1$ to $C_3$ fraction of the gas calculated from the spectrometer analyses increased with coal rank as shown in table 2. Although the gas formed from low-rank coals contained less methane, there were more higher hydrocarbons present which gave a higher heating value. This trend extends to the oils produced; that is, the low-rank coals produced more liquid product as shown in figure 6. Anthracite and char produced no liquid products.

TABLE 2.- Distribution of light hydrocarbons in the gas

| | Composition, vol pct | | |
| | Methane | Ethane | Propane |
|---|---|---|---|
| Lignite ............... | 82 | 15 | 3 |
| High volatile C ....... | 88 | 10 | 2 |
| High volatile A ....... | 90 | 9 | 1 |
| Anthracite ........... | 92 | 7 | 1 |
| High volatile C char .. | 92 | 8 | 0 |

An analysis of the liquid product from a Wyoming coal (hvcb) is shown in table 3. The mass spectrum indicates a complex mixture of products containing aromatics and tar acids. Analyses of the liquids from lignite and Pittsburgh seam coal (hvab) were almost identical to the results shown for the hvcb Wyoming coal.

TABLE 3.- Mass spectra of oils from hydrogenation of a Wyoming coal (hvcb)
(6,000 psig, 800° C)

| Possible compound types including alkyl derivatives | Volume-percent of total oil |
|---|---|
| Benzene, toluene, etc. ...... | 23.1 |
| Phenols ..................... | 21.5 |
| Naphthalenes ................ | 18.7 |
| Indanols .................... | 11.0 |
| Phenanthrenes, anthracenes .. | 3.3 |
| Balance ..................... | 22.4 |

The next subject describes some work that falls in the category of unexpected findings. When anthracite coal was hydrogenated for making high-Btu gas, the cold trap contained a yellow powder identified by ultraviolet analysis as a high concentration of coronene.

The experimental data shown in table 4 indicate the limits for temperature and pressure - 6,000 to 8,000 psig and 700° to 800° C. The maximum yield of coronene was 0.8 wt pct of the low-volatile (4.2 percent volatile matter) anthracite. The product was a low-density, porous yellow-orange solid that was about 70 percent coronene by ultraviolet analysis. Some samples contained over 80 percent coronene. The balance is mostly 1,12-benzperylene and pyrene. Most of the coronene was recovered in the cold trap, but some was obtained from the connecting lines and reactor by washing with warm benzene. Coronene in the wash is included in the yield.

TABLE 4.- Coronene from hydrogenation of anthracite

| 30 minutes at - | | Coronene, weight-percent | |
| Temperature, °C | Pressure, psig | In solid product | Of maf coal |
|---|---|---|---|
| 600 | 6,000 | 0 | 0.01 |
| 700 | 6,000 | 71 | 0.5-0.8 |
| 800 | 6,000 | 37 | 0.3 |
| 600 | 8,000 | 0 | 0 |
| 700 | 8,000 | 49 | 0.5-0.7 |
| 800[1] | 8,000 | 38-54 | 0.4-0.5 |
| 700 | 3,000 | 50(est) | 0.08 |

[1] 15 minutes.

Coronene could also be produced from Pittsburgh seam coal (hvab), but from the few experiments made it appeared that the higher temperature of 800° C at 6,000 psig was required to yield the same amount of coronene - about 0.5 wt pct of the maf coal. However, no dry solids were recovered in the cold trap, and the yields are based on an analysis of the benzene washings. Equal quantities of coronene and pyrene were found when a hvab coal was used.

Other materials such as asphaltenes and centrifuge residue from the hydrogenation of coal were also examined. The yields of coronene were lower and 4 to 10 times more pyrene were present. Thus, no other coal or coal hydrogenation product was as good as anthracite for this synthesis. Since the yield of coronene from coal is only 0.5 to 0.8 percent, a use must be found for the resulting hydrocarbon gases and char. It has been estimated that if the gas and char are sold for fuel value, the coronene could be sold for less than $1 a pound.

Another product that can be considered is the mixture of closely related chemicals that may be used as fuel for supersonic aircraft. The distillable oil from the hydrogenation of coal contains bicyclic aromatics that could be hydrogenated to naphthenes that are thermally stable and have many desirable properties. An oil produced in the pilot plant of the Bureau of Mines was distilled to 325° C end point oil for feed stock. This oil was then desulfurized and partially hydrogenated over cobalt-molybdate catalyst at 2,500 psig, 400° C, 50 scf $H_2$ per pound of oil, and at a space velocity of 3 vol oil/hr/vol catalyst. A 180° to 280° C fraction of the desulfurized oil was saturated over a nickel catalyst to produce a naphthenic product.

A similar fuel for supersonic jet aircraft has been produced from a distillable fraction of tar made by low-temperature carbonization. Results of this work have been published in a Report of Investigations.[10] In figure 8 the narrow distribution of products indicated by mass spectrometer analysis is shown. Practically all of the oil is in the $C_{10}$ to $C_{15}$ range with a maximum at $C_{12}$ or $C_{13}$. This fuel met all but one of the specifications established tentatively for this type of fuel. For some as yet unexplained reason, this oil was not stable in the high-temperature test unit. However, recent laboratory tests indicate that the oil is more stable after rehydrogenation.

A plasma jet unit is now being used for experiments with coal at very high temperatures. If the temperature of the coal approaches the plasma temperature, extremely severe hydrogenation conditions can be established.

At the present time only limited results are available. When coal is heated in an argon plasma, the products are a very fine residue, carbon monoxide, methane, acetylene, hydrogen, and nitrogen. The composition shown in table 5 was obtained with slow cooling of the products. Quenching with gas or liquids will give other products. Also, the products will vary with other operating variables such as the working gas composition, gas and coal rates, and power input.

Other forms of energy such as microwaves, corona discharge, and maser and laser beams have also been considered as an active environment for coal hydrogenation experiments. However, manpower and financial limitations are keeping these in the paper stage at the present time.

Several important factors are becoming evident as work on hydrogenation of coal continues. The system is being modified to yield fewer products. Instead of a wide range of liquid fuels we have been making hydrocarbon gases and light aromatics, relatively pure polycyclic products, and relatively narrow fractions. Hydrogenation yields more of these desired products than a carbonization or coking process. Thus, hydrogenation provides us with a potential for providing large quantities of useful products when a profitable demand develops. Many people envision a coal hydrogenation product "tree" as extensive as the popular "tree" published for coal tar. The Bureau of Mines will continue to do its part in providing an atmosphere in which the hydro-

genation tree will come to fruition.

TABLE 5.- Gas composition from coal in a plasma jet
(5 kw net power input, hvab coal 70 x 100 mesh)

| | | |
|---|---|---|
| Argon .............. | 84.5 | - |
| Hydrogen .......... | 9.3 | 60 |
| Nitrogen .......... | 0.9 | 6 |
| $CH_4$ .............. | 0.3 | 2 |
| $C_2H_2$ ............. | 2.3 | 15 |
| CO ............... | 2.7 | 17 |
| $CO_2$ .............. | tr | - |

Coal conversion - 15 percent
Residue ($<$ 325 mesh) - 6 percent of coal feed

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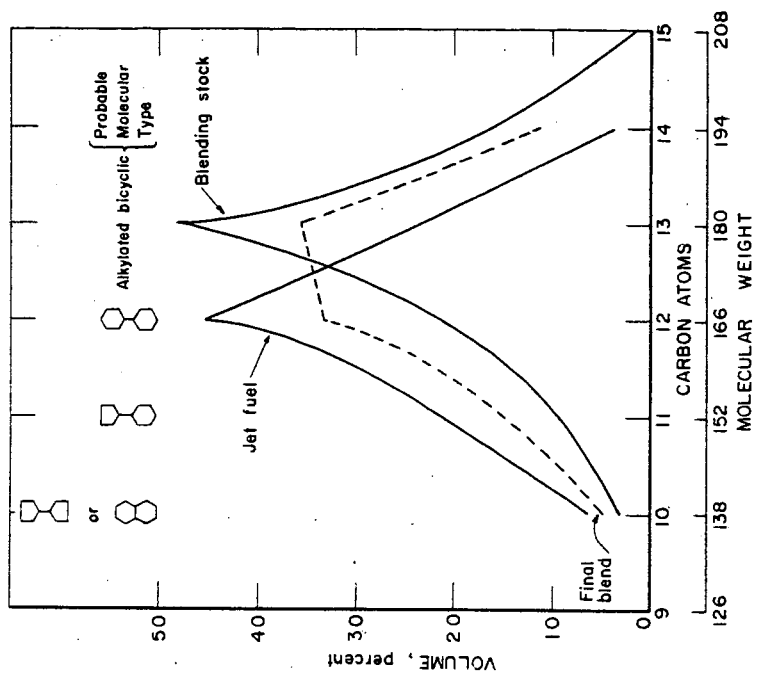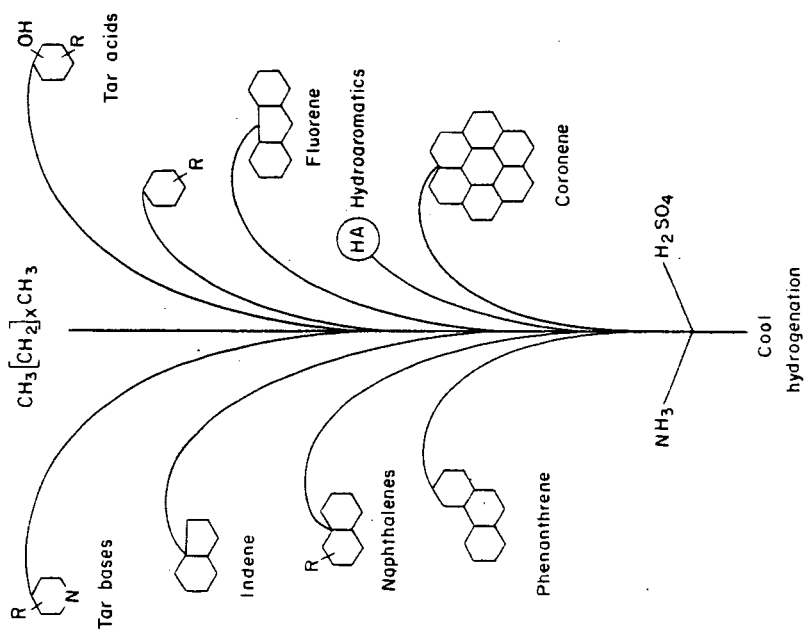
Figure 8.- Molecular weight distribution in jet fuels.



Figure 1.- Typical chemicals from hydrogenation of coal.
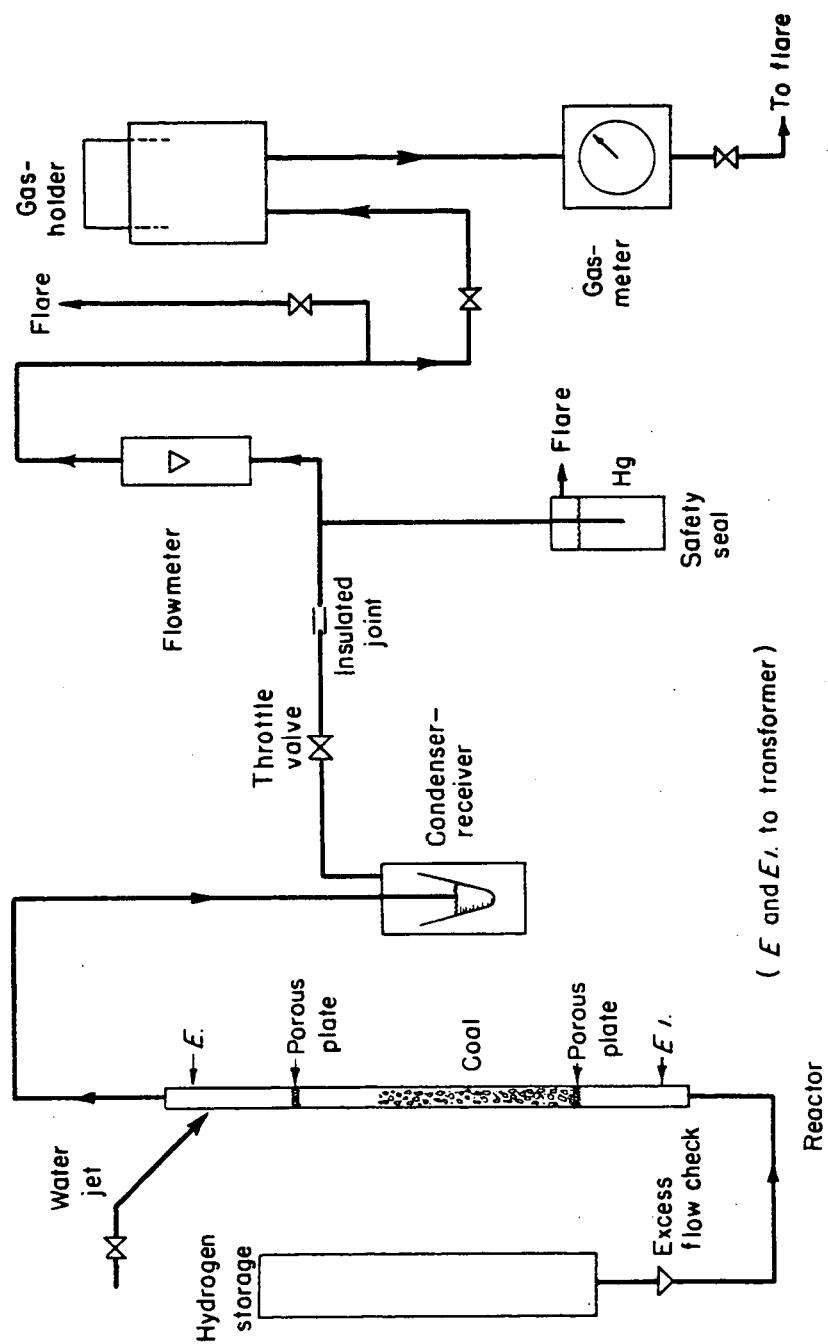
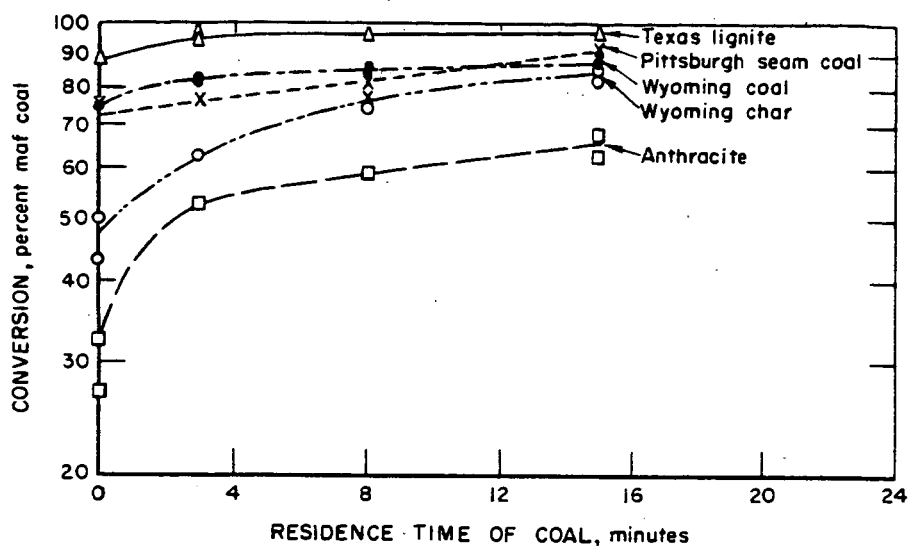Figure 3.—Simplified flow sheet of apparatus.

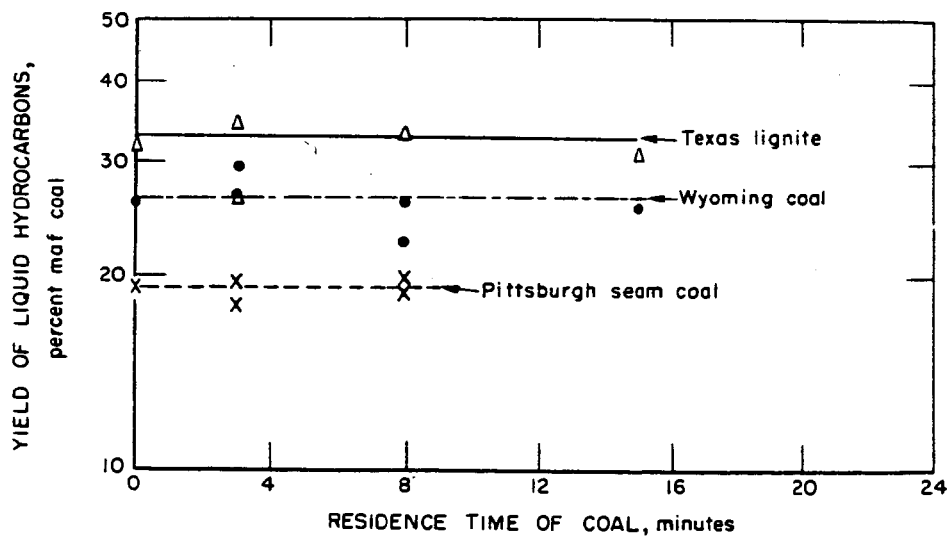Figure 4.- Effect of residence time on conversion.



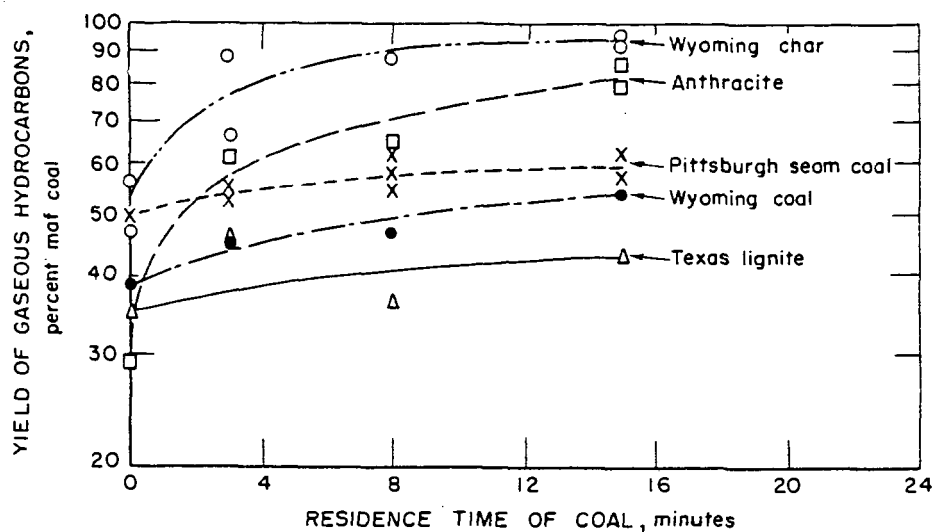Figure 6.- Effect of residence time on yield of liquid hydrocarbons.

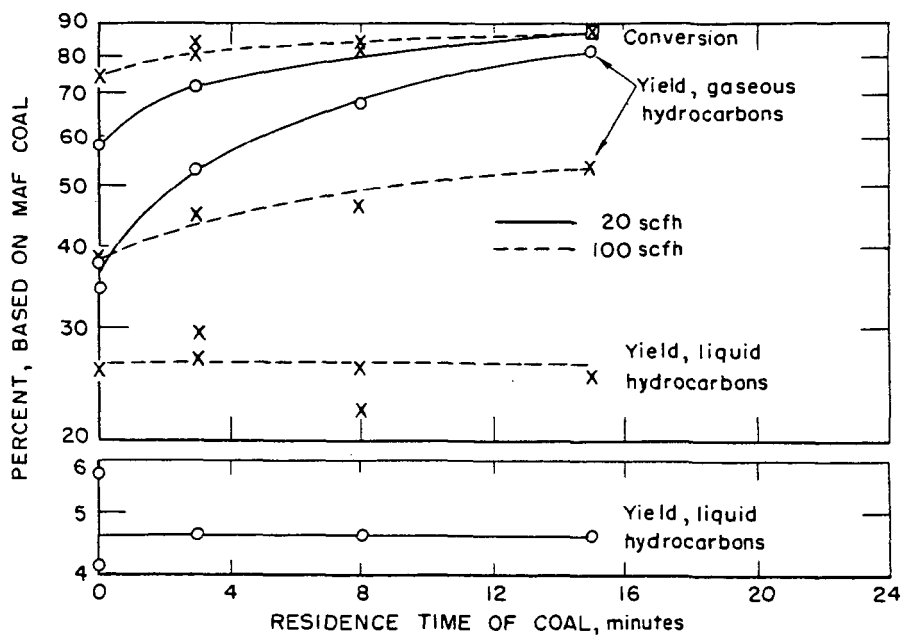Figure 5.—Effect of residence time on yield of gaseous hydrocarbons.



Figure 7.— Effect of residence time on product distribution for Wyoming coal at two gas rates.